A Systematic Investigation and Insight into the Formation Mechanism of Bilayers of Fatty Acid/Soap Mixtures in Aqueous Solutions

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Supporting Information

ABSTRACT: Vesicles are the most common form of bilayer structures in fatty acid/soap mixtures in aqueous solutions; however, a peculiar bilayer structure called a "planar sheet" was found for the first time in the mixtures. In the past few decades, considerable research has focused on the formation theory of bilayers in fatty acid/soap mixtures. The hydrogen bond theory has been widely accepted by scientists to explain the formation of bilayers. However, except for the hydrogen bond, no other driving forces were proposed systematically. In this work, three kinds of weak interactions were investigated in detail, which could perfectly demonstrate the formation mechanism of bilayer structures in the fatty acid/soap mixtures in aqueous solutions. (i) The influence of hydrophobic interaction was detected by changing the chain length of fatty acid (C_{n+1}H_{2n+1}COOH), in which n = 10 to 18, the phase behavior was investigated, and the phase region was presented. With the help of cryogenic transmission electron microscopy (cryo-TEM) observations, deuterium nuclear magnetic resonance (\textsuperscript{2}H NMR), and X-ray diffraction (XRD) measurements, the vesicles and planar sheets were determined. The chain length of C_{n+1}H_{2n+1}COOH has an important effect on the physical state of the hydrophobic chain, resulting in an obvious difference in the viscoelasticity of the solution samples. (ii) The existence of hydrogen bonds between fatty acids and their soaps in aqueous solutions was demonstrated by Fourier transform infrared (FT-IR) spectroscopy and molecular dynamical simulation. From the pH measurements, the pH ranges of the bilayer formation were at the pK\textsubscript{a} values of fatty acids, respectively. (iii) Counterions can be embedded in the stern layer of the bilayers and screen the electrostatic repulsion between the COO\textsuperscript{-} anionic headgroups. FT-IR characterization demonstrated a bidentate bridging coordination mode between counterions and carboxylates. The conductivity measurements provided the degree of counterion binding (\beta = 0.854), indicating the importance of the counterions.

INTRODUCTION

There are 40 different kinds of naturally occurring fatty acids, which are the key components of lipids. Fatty acid soaps, a general term for the "salt" of fatty acids, which can be easily produced via a neutralization reaction between a fatty acid and an alkali liquid (KOH, NaOH, etc.), are important chemical raw materials and still valuable in recent studies. In 1973, Gebicki\textsuperscript{1} investigated the oleic acid soap system and made the first observation of fatty acid vesicles with the help of freeze-fracture TEM (FF-TEM). In fact, fatty acid soaps were widely studied previously. The phase behavior of sodium stearate in water\textsuperscript{2} and organic solvent,\textsuperscript{3} as well as the stability of sodium stearate gels,\textsuperscript{4} was investigated in the 1940s. The solubility and aggregates in solutions were not presented clearly. With the development of new techniques, such as cryo-TEM, FF-TEM, etc., the microstructures can be easily observed nowadays.

In recent decades, the formation mechanism of the bilayers in fatty acid soap systems has become a popular topic. Hydrogen bonds play a vital role in the formation of these fatty acid bilayers\textsuperscript{7-9}. It is well known that the phase behavior of the fatty acid soap system depends on the ionization state of the carboxyl headgroup.\textsuperscript{10} Cistola et al. investigated the phase behavior of fatty acids at half-ionization as a function of water content and temperature\textsuperscript{11} and the phase behavior as a function of ionization state of the carboxyl group,\textsuperscript{12} respectively. They found that the pH for the formation of the bilayers in fatty acid solutions was in the range of 7–9. Later, Shah\textsuperscript{13} investigated the pK\textsubscript{a} of fatty acids with different chain lengths, in which they found that hydrogen bonds were easily constructed when the pH was near the pK\textsubscript{a}. In 2007, Walde presented a review entitled “Fatty Acid Vesicles”, in which the authors summarized the previous literature and discussed the features of fatty acid vesicles and the application as a protocell model.\textsuperscript{14} However, to the best of our knowledge, the formation mechanism of bilayers was just limited at the hydrogen bond theory, and no direct
(hydrogen bonds, hydrophobic interactions, and electrostatic interactions). Because of the three interactions, the fatty acid molecules stack together and form vesicles and planar sheets at different $p$ values, respectively. The stern layer model is applied to elaborate the structure of the bilayers in detail. The hydrophobic force drives the primary structure of the bilayers, and hydrogen bonds shorten the distance between headgroups. Most of the counterions (>80%) enter the stern layer of the bilayers, screen the electrostatic repulsion between the headgroups, and further shorten the distance between headgroups. From the combination of the three weak interactions, the bilayers exist stably. The solutions are thermodynamic stable and do not change for at least 1 year.

### CONCLUSIONS

In this study, we investigated the formation mechanism of the bilayers in fatty acid soap systems in detail. First, the phase behavior and the microstructures were investigated systematically. Except for the common vesicle structure, a planar sheet structure was observed with an increase in chain length. On this basis, hydrogen bonding was demonstrated by pH measurements, FT-IR, and molecule dynamical simulation. Electrostatic interaction was determined by the coordination mode of counterions and the degree of counterion binding. Hydrophobic interaction was detected by changing the chain length. The physical state of the hydrophobic chain was determined by DSC and rheological measurements. Finally, the packing parameter ($p$) was estimated for different aggregates. Considering the wide application of fatty acids in the cosmetic industry, we expect the results from the current study to be of practical interest.

### ASSOCIATED CONTENT

*Supporting Information*

Data for XRD characterization, cryo-TEM images, rheograms, pH measurements, metal−carboxylate coordination mode, and FT-IR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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### REFERENCES


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**Scheme 1. Proposed Mechanism for the Formation of Different Bilayer Structures**

“The purple, red, and the blue spheres represent Cs+ and protonated and deprotonated fatty acid molecules, respectively. The hydrophobic tail is represented by green lines.


